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Termination Reaction in the Anionic Polymerization of Methacrylonitrile

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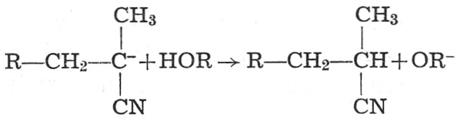
The anionic polymerization of methacrylonitrile initiated by triethylphosphine in dimethylformamide was studied. Experimental evidence for two mechanisms of termination reaction was obtained. By addition of water or alcohol in polymerizing system the rate of polymerization and molecular weight of polymethacrylonitrile decrease, which proves the termination reaction to be bimolecular and proceed by interaction of the active carbanion with water or alcohol. The rate constant for termination of free anions with water was determined, $k'_{H_2O} = 2.2 \times 10^2$ dm^3 mol^{-1} s^{-1}. The termination reaction could not be excluded by purification and prolonged drying of all components of the system, which indicates that the second mechanism of termination is operative as well. Conductivity measurements gave evidence for a monomolecular spontaneous reaction leading to deactivation of the anion.

INTRODUCTION

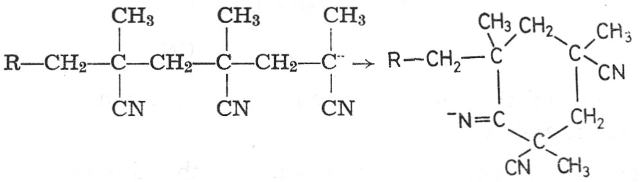
In the anionic polymerization of acrylonitrile and methacrylonitrile, two mechanisms were proposed for the termination reaction:

a) termination by compounds containing hydroxyl groups



$$R{-}CH_2{-}\underset{CN}{\overset{CH_3}{C^-}} + HOR \rightarrow R{-}CH_2{-}\underset{CN}{\overset{CH_3}{CH}} + OR^-$$

b) spontaneous termination by intramolecular cyclization[1,2]



Evidence for the first mechanism is the decrease of the rate of polymerization when water is added to the polymerization system. The second mechanism was proposed on the basis of infrared evidence for the presence of carbonyl group within the polymer molecule. It is assumed that the cyclization may occur as a result of the interaction of the growing carbanion with the positive carbon of the nitrile group giving a stable six-membered ring. The imine anion is not able to initiate polymerization and on termination of the polymerization with acidic methanol the C=NH group is formed, which is hydrolized to the carbonyl group, the cyclic ketone in this case. However, infrared evidence shows that the carbonyl group is present in the form of acid amide[2].

So it could not be established whether carbonyl is formed by hydrolysis of $(C=N)_x$ groups (obtained after further cyclization of the imine anion with the pendant nitrile groups) or by direct hydrolysis of the nitrile group.

Our present work on anionic polymerization of methacrylonitrile initiated by triethylphosphine gives new evidence in favour of the spontaneous termination reaction. Investigation of the polymerization in the presence of water enabled us to determine the rate constant of termination by water.

EXPERIMENTAL

Methacrylonitrile and dimethylformamide were purified by the usual method, dried over calcium hydride, distilled and stored in vacuum over calcium hydride. Monomer and solvent were redistilled in vacuum before use. Triethylphosphine was prepared as described elsewhere[3].

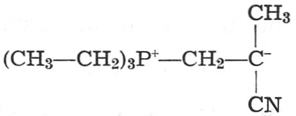
Polymerization was carried out at 40.8 °C in vacuum or in argon atmosphere. In the latter case triethylphosphine diluted with dimethylformamide was injected into the monomer solution.

The water was added to the system by condensation from the vapour phase. The concentration of water was determined from the pressure of water vapour prior to condensation.

Kinetics of polymerization was followed dilatometrically. For conductivity measurements a special dilatometer containing electrodes was used. The molecular weight of the polymer was determined viscosimetrically.

RESULTS AND DISCUSSION

The anionic polymerization of methacrylonitrile initiated by triethylphosphine in dimethylformamide proceeds via zwitter-ion mechanism[4,5]. Analysis by n. m. r. spectroscopy on ^{31}P and ^{1}H as well as elemental analysis prove that in the intiation process the following zwitter-ion structure is formed:



$$(CH_3{-}CH_2)_3P^{+}{-}CH_2{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CN}{C^{-}}}$$

The initiation reaction is slow. Addition of monomer to the carbanion leads to macrozwitter-ion.

Two experimental facts are imoprtant for the discussion of the termination mechanism:

1. By addition of water or alcohol the rate of polymerization and molecular weights of the polymer are decreased (Table I).

TABLE I

Effect of water on polymerization rate and molecular weight of polymethacrylonitrile

$[(C_2H_5)_3P] = 10^{-2}$ mol/dm^3, [MAN] = 2.1 mol/dm^3, $t = 40.8$ ^{0}C

$[H_2O] \times 10^4$ mol/dm^3	Rate of polymerization $^0/_0$/minute	Molecular weight
not added	5.1	1.4×10^6
2	3.1	4.5×10^5
4	2.3	2.5×10^5
6	1.7	1.7×10^5
8.5	1.4	1.2×10^5

2. The termination reaction could not be excluded by purification and prolonged drying of all components of the system. This means that besides termination with water some mechanism of spontaneous termination should be also active.

Valuable information about the termination reaction in zwitter-ion polymerization can be obtained by conductivity measurements. It could be expected that in zwitter-ion polymerization the growing chains will not influence markedly the conductivity of the polymerizing system, because in zwitter-ions the opposite charges are covalently bound to each other.

On the other hand, in the presence of the terminating agent, ion pairs or separated ions are produced, *i. e.* the counterions are no more covalently bound. The concenration of these ions increases during the course of polymerization because the initiation reaction is slow in the system. In this case the conductivity should increase during the polymerization.

The results of conductivity measurements in dry polymerizing systems and in presence of a terminating agent are plotted in Fig. 1.

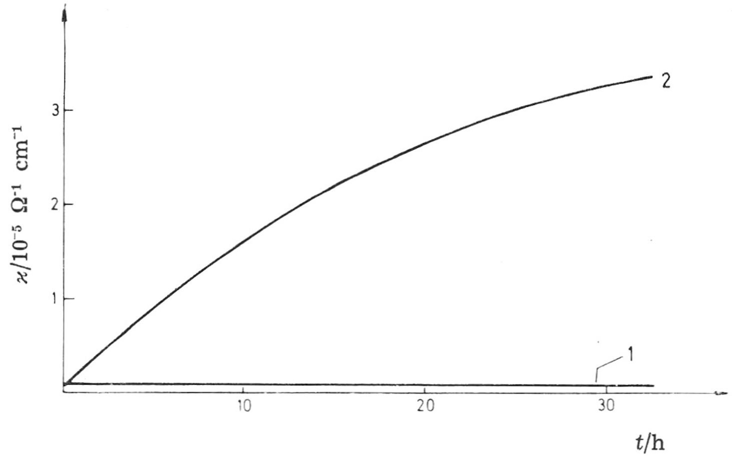


Fig. 1. The change of conductivity during polymerization: Curve 1 — Polymerization in dry system, total conversion — 92$^0/_0$; Curve 2 — Polymerization in the presence of water, total conversion — 45$^0/_0$; $[(C_2H_5)_3P] = 10^{-2}$ mol/dm^3, [MAN] = 4.3 mol/dm^3, $[H_2O] = 3 \times 10^{-3}$ mol/dm^3

It can be seen that in the dry systems there is no increase of conductivity (curve 1), whereas conductivity increases during the reaction in the presence of water (curve 2). On the basis of these results we can accept two proposed mechanisms of termination reaction:

1. Bimolecular termination by interaction with water.
2. Monomolecular spontaneous reaction leading to deactivation of the anion (probably by intramolecular cyclization and transfer of electron to nitrogen).

Only in the case of monomolecular termination and conservation of deactivated anion on the terminated polymeric chain, does the termination reaction not influence the conductivity of the polymerizing system. If chain transfer reaction, leading to the covalently not bound ionic structures, would dominate, the conductivity should increase. Accordingly, the results of conductivity measurements as well as the dependence of molecular weight of the polymer on monomer concentration[6] prove that there is no chain transfer reaction in the system.

Investigation of polymerization kinetics in »dry« systems and in presence of water enabled us to determine the termination rate constants.

The results for dry systems were published elsewhere[7,8]. It was shown that two types of active species exist in the system: free ions and ion pairs. They are in equilibrium, the equilibrium constant depending on the degree of polymerization. Ion pairs are practically inactive in polymerization. Taking into account slow initiation, monomolecular equilibrium between ion pairs and free ions, fast growth reaction only on free ions and termination of ion pairs and free ions, the initial rate for stationary concentration of active centres in macrozwitter-ion polymerization is given by the equation

$$W_0 = \frac{k_i k_- [C]_0 [M]_0^2}{k'_t} \exp\left(-2k_t/k_- K_d^{(1)} [M]_0\right) \qquad (1)$$

where $[C]_0$ is the initial concentration of triethylphosphine $[M]_0$ is the initial concentration of methacrylonitrile, k_i, k_-, k'_t and k_t are the rate constants for initiation, chain growth and termination on free ions or ion pairs, respectively. $K_d^{(1)}$ is the equilibrium constant ion pairs-free ions for the degree of polymerization equal to 1.

From Eq. 1, the equation for the initial rate of macrozwitter-ion polymerization in the presence of water can easily be obtained:

$$W_0 = \frac{k_i k_- [C]_0 [M]_0^2}{k'_t + k'_{H_2O} [H_2O]} \exp \frac{-2\,(k_t + k_{H_2O} [H_2O])}{k_- K_d^{(1)} [M]_0} \qquad (2)$$

After rearrangement of Eq. 2:

$$\frac{[C]_0 [M]_0^2}{W_0} = \frac{k'_t + k'_{H_2O} [H_2O]}{k_i k_-} \exp \frac{2\,(k_t + k_{H_2O} [H_2O])}{k_- K_d^{(1)} [M]_0} \qquad (3)$$

and plotting $\frac{[C]_0 [M]_0^2}{W_0}$ *versus* $[H_2O]$ according to Eq. 3, linear dependence was obtained (Fig. 2).

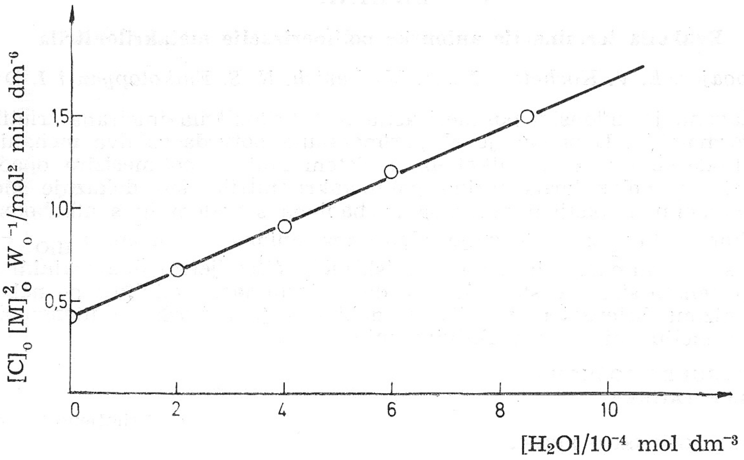


Fig. 2. Reciprocal rate of polymerization versus concenration of water; $[(C_2H_5)_3P] = 10^{-2}$ mol/dm^3, [MAN] = 2.1 mol/dm^3

This means that termination of ion pairs by reaction with water is negligible. This results is consistent with our finding that ion pairs are practically unreactive also for monomer addition. The reason for such behavior could be the strong shielding of the active center in the ion pair by substituents on the carbon and phosphorus atoms.

Using the values for rate constants obtained by investigation of the polymerization in a dry system, we determined the rate constant for termination of free ions with water from the slope of the straight line in Fig. 2:

$$k'_{H_2O} = 2.2 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

Since the propagation rate constant is only two times higher than the obtained rate constant for termination with water, high molecular weight polymethacrylonitrile can be obtained only after rigorous drying of all the components of the polymerizing system. For instance, the quantity of water in the polymerizing system must be less than 0.001% to obtain a degree of polymerization of 10^4.

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SAŽETAK

Reakcija terminacije anionske polimerizacije metakrilonitrila

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Proučavana je anionska polimerizacija metakrilonitrila inicirana trietilfosfinom u dimetilformamidu. Dobivena je eksperimentalna potvrda za dva mehanizma terminacije. Dodatkom vode ili alkohola u sistem koji se polimerizira opada brzina polimerizacije i molekularna težina polimetakrilonitrila, što dokazuje biomolekularnu terminaciju, reakcijom aktivnog karbaniona s vodom ili s alkoholom. Određena je konstanta brzine reakcije slobodnog aniona s vodom, $k'_{H_2O} = 2,2 \times 10^2$ dm^3 mol^{-1} s^{-1}. Terminaciju je nemoguće isključiti čišćenjem i dugotrajnim sušenjem svih komponenata sistema, što pokazuje da se terminacija odvija i po nekomu drugom mehanizmu. Mjerenjem vodljivosti dobivena je potvrda za monomolekularnu spontanu reakciju kojom se deaktivira anion.

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